

SYNTHESIS AND CHARACTERIZATION OF HYDROXYL TERMINATED  
EPOXIDIZED NATURAL RUBBER AS A BINDER FOR SOLID ROCKET  
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EPOXIDIZED NATURAL RUBBER AS A BINDER FOR SOLID ROCKET  
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I declare that this thesis entitle “*Synthesis and Characterization of Hydroxyl Terminated Epoxidized Natural Rubber as a Binder for Solid Rocket Propellant*” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any degree.

Signature :.....

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Date : 01 August 2016

To my beloved parents, husband, kids and family

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## ABSTRACT

Hydroxyl terminated epoxidized natural rubber (HTENR) was synthesized via oxidative degradation method to produce a low molecular weight rubber intended for use as a binder for solid rocket propellant. Epoxidized natural rubber (ENR) was depolymerized via chemical degradation method using cobalt (II) acetylacetonate (CAA) as the oxidizing agent, followed by treatment with sodium borohydride as a reducing agent to introduce hydroxyl (OH) functional group at both chain ends. The reaction times and the amount of oxidizing agent were varied from 1 h to 20 h and 1% to 5% w/w of CAA respectively in order to obtain the low molecular weight of HTENR. The molecular weight of HTENR was determined using gel permeation chromatography (GPC). The lowest molecular weight of HTENR was achieved at 3% w/w of CAA after 5 hours reaction time at 60°C where  $M_n$  and  $M_w$  were 34000 g/mol and 62000 g/mol respectively. FTIR analysis confirmed that HTENR contained OH group with the appearance of a broad peak around 3200-3600  $\text{cm}^{-1}$  after the reaction. The presence of OH end groups was verified by NMR analysis with the appearance of two peaks at 3.38 ppm and 3.88 ppm corresponding to methylene proton adjacent to hydroxyl group in  $\text{HOCH}_2\text{CH}_2\text{CH}_2-$  and methine proton adjacent to OH group in  $-\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ , respectively. HTENR with different  $M_n$  were used to produce propellant and its burning rate and calorific value were compared with HTPB based propellant as a reference. Although HTENR based propellant produced a slightly lower burning rate compared to that of HTPB based propellant, its combustion energy produced was relatively similar to HTPB based propellant. Therefore, it is expected that HTENR is suitable to be used as a binder in solid rocket propellant.

## ABSTRAK

Getah asli epoksida berterminal hidroksil (HTENR) telah disintesis menggunakan kaedah penguraian oksidatif bagi menghasilkan getah dengan berat molekul rendah sebagai pengikat pendorong roket pepejal. Getah asli epoksida (ENR) dinyahpolimer melalui kaedah penguraian kimia menggunakan kobalt (II) asetil asetonat (CAA) sebagai agen pengoksidaan diikuti dengan rawatan menggunakan natrium borohidrid sebagai agen penurunan bagi menghasilkan kumpulan hidroksil (OH) pada hujung kedua-dua rantai. Kesan masa tindak balas dan kuantiti bahan pengoksidaan diubah dari 1 jam ke 20 jam dan dari 1% ke 5% w/w CAA bagi menghasilkan molekul dengan berat terendah. Kromatografi penyerapan gel (GPC) diguna untuk menentukan berat molekul HTENR. HTENR dengan berat molekul terendah diperolehi pada 3% w/w CAA selepas 5 jam tindak balas pada 60°C dengan  $M_n$  dan  $M_w$  masing-masing adalah 34,000 g/mol dan 62,000 g/mol. Analisis FTIR membuktikan bahawa HTENR mengandungi kumpulan OH dengan kewujudan puncak lebar sekitar 3200-3600  $\text{cm}^{-1}$ . Kewujudan kumpulan berfungsi OH di hujung kedua-dua rantai HTENR dikesan menggunakan analisis salunan magnet nuklear (NMR) dengan kemunculan dua puncak pada 3.38 ppm dan 3.88 ppm yang merujuk kepada proton metilena bersebelahan dengan OH dalam  $\text{HOCH}_2\text{CH}_2\text{CH}_2-$  dan proton metin bersebelahan dengan OH dalam  $-\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ . Bahan dorongan pepejal dihasilkan daripada HTENR dengan berat molekul berbeza dan kadar pembakaran dan nilai kalori dibezakan dengan pendorong berasaskan HTPB sebagai rujukan. Walaupun pendorong HTENR menghasilkan kadar pembakaran yang sedikit rendah berbanding pendorong HTPB, tenaga pembakaran yang dihasilkan adalah hampir sama. Kesimpulannya, HTENR sesuai untuk digunakan sebagai pengikat pendorong roket pepejal.

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**LIST OF ABBREVIATIONS**

Al	-	Aluminum
AN	-	Ammonium nitrate
AP	-	Ammonium perchlorate
CTPB	-	Carboxy terminated polybutadiene
DPNR	-	Deproteinized natural rubber
ENR	-	Epoxidized natural rubber
FTIR	-	Fourier transform infrared
GPC	-	Gel permeation chromatography
HTNR	-	Hydroxy terminated natural rubber
HTPB	-	Hydroxy terminated polybutadiene
IPDI	-	Isophorone diisocyanate
KBr	-	Potassium bromide
LNR	-	Liquid natural rubber
$M_n$	-	Number average molecular weight
$M_w$	-	Weight average molecular weight
MWD	-	Molecular weight distribution
NMR	-	Nuclear magnetic resonance
NR	-	Natural rubber
NRL	-	Natural rubber latex
PBAN	-	Poly (butadiene-acrylonitrile)
SBR	-	Styrene butadiene rubber
SMR	-	Standard Malaysia Rubber
TDI	-	Toluene diisocyanate
THF	-	Tetrahydrofuran
TLNR	-	Telechelic liquid natural rubber

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## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Introduction**

Composite solid rocket propellants are basically prepared from a mixture of rubber binder, curing agent, oxidizer and metal fuel. The rubber binder is an important ingredient comprises in composite solid rocket propellants. It is not only functioning as a binder to hold all ingredients together but also behaves as a high energy fuel owing to hydrogen and carbon compounds as polymer backbones. The high hydrogen over carbon (H/C) ratio of long polymer chains are believed to produce higher combustion energy and highly preferred as a fuel (Jain, 2002) due to the availability of energy stored in the hydrocarbons (Bluestone, 2010). Thus, the use of hydrocarbon based binder is a value added to composite solid rocket propellants application. Amongst the earliest rubber binder used are polysulfides, polystyrene, epoxy resins and polyurethanes (Daniel, 2006). Polysulfide was the first liquid polymer that could be converted to a rubbery solid by a simple chemical reaction as a binder in composite solid rocket propellant owing to its excellent physical properties and superior towards the effect of oxygen, ozone, and moisture. Although the presence of sulfur in the polymer backbones that behave as an oxidizer leads to production of high specific impulse during combustion process (Ang and Pisharath, 2012), it may decrease the performance of solid propellant as well.

The low temperature property of polysulfide binder which is not sufficient for solid propellant application becomes its major drawback. Many attempts have been done to improve this property including the addition of silanes (Schwarz and Lowrey, 1967), formation of butyl formal polysulfide and butyl ether polysulfide (Gonser, 2003). Moreover, upon curing of polysulfide binder with metal oxides, the addition of metallic fuel powder should be avoided since it may eliminate water thus affected the physical and ballistic properties of solid propellant. In order to enhance the rocket performance while reducing its burning temperature, liquid polybutadiene (PB) polymers has been used to substitute of polysulfide in solid rocket propellant application (Daniel, 2006).

Since then, three types of PB polymers that widely used in solid rocket propellant were poly (butadiene - acrylic acid) copolymers (PBAA), poly (butadiene - acrylic acid - acrylonitrile) terpolymers (PBAN), and carboxyl terminated polybutadiene (CTPB). The copolymer of butadiene and acrylic acid (PBAA) with random distribution of  $-COOH$  groups in the polymer chain enables it to react with an epoxy resin forming a cured binder thus improves the specific impulse and mechanical properties with the exception of poor tear strength. The poor tear strength of PBAA binder was solved by the addition of acrylonitrile yielding of PBAN (Agrawal, 2010). This new rubber binder exhibit improved properties compared to the previous binders and relatively cheaper to produce (Manu, 2014 and Bluestone, 2010). Afterwards, CTPB with better mechanical properties and low temperature characteristic has been discovered in the late 1950s to substitute the earlier binders. Unfortunately, the main problem with CTPB is occurred upon curing whereby the ammonium perchlorate (AP) would interfere with the curing agents (Klager, 1984).

Further, another rubber binder that extensively used in composite solid rocket propellants derived from polyurethanes family was developed consisting of diols with hydroxyl terminated end groups which were then cured with diisocyanates to form urethane network. Similar to polysulfide binder, liberation of water during the reaction of rubber binder with isocyanates may affect the performance of solid

propellants thus strictly forbidden. In addition, the presence of some oxygen in the polyurethanes binder system has contributed to exhibit high energetic performance compared with polysulfide binder (Gonser, 2003). Although with these improvement, CTPB remained favorable. Only after the first test of HTPB in solid rocket propellant application demonstrated higher strain capacity at low temperature and improves ageing properties over CTPB, the exploitation of CTPB has been abandoned. Since that HTPB become extensively used in military and space application and remained wanted.

HTPB has been used extensively over five decades ago as a rubber binder in composite propellant application (Bluestone, 2010 and Daniel, 2006) since it was first tested in rocket motor. Many studies have been done on the synthesis and characterization of HTPB as a binder for propellant application as well. HTPB is reported to be the only prepolymer synthesized as a binder for solid rocket propellant application (Jain, 2002 and Sekkar and Raunija, 2015). HTPB are prepared by the free radical polymerization of butadiene, using hydrogen peroxide as initiator and an alcohol as solvent. This prepolymer could serve as a binder as well as a high energy fuel. HTPB exhibits good ageing properties for long storage time and low glass transition temperature ( $T_g$ ).

Among others PB based binder, HTPB become the workhorse due to fairly good mechanical properties, safety, easy handling, low cost and moderately high burning rate. It is a viscous prepolymer with hydroxyl end groups that suitable for chain extension reaction with addition of a curing agent (Jain, 2002) to be function as a binder in solid rocket propellant. Many types of isocyanate curing agent have been used such as aliphatic isocyanates and aromatic isocyanates. HTPB can be cured at lower temperature and required minimum curing time make it distinguishable to other types of PB binder. In spite of the advantages offered by HTPB, developments of new rubber binder as a replacement is needed to either improve the mechanical properties or rocket motor performance. It is an advantageous to discover an alternative binder with comparable properties to replace HTPB especially derived from natural resources.



Another potential rubber binder for solid rocket propellant application derived from natural rubber (NR) namely hydroxyl terminated natural rubber (HTNR) has been reported earlier (Gupta *et al.*, 1985; Thomas *et al.*, 1992; Onn, 2014; Jaafar, 2014; Ab. Rasid, 2015 and Baharulrazi, 2015). HTNR propellant was reported to produce high mechanical and ballistic properties relative to HTPB propellant (Gupta *et al.*, 1985). Accordingly, the development of HTNR propellant with addition of 30 – 37.7% of metallic fuel resulted in superior mechanical and thermal properties in contrast to HTPB propellant (Thomas *et al.*, 1992). Based on the previously reported data, it is believed that HTNR binder is an ideal candidate to substitute HTPB binder. Aside from being natural resources, the wide source of availability become the major advantage of choosing NR as a rubber binder since it is renewable resources as well. Above all, development of a new rubber binder from NR based resources is seemed valuable to be produced as an alternative.

## **1.2 Research Background**

Rubber binders for composite solid propellants are basically produced from a hydrocarbon polymer which consists of hydrogen and carbon chain. The longer rubber chains show the higher combustion energy due to energy store in the polymer chains. The development of polyurethanes binder in the early 1950s has emerged to overcome the main drawback of the existing rubber binder such as poor mechanical properties, insufficient low temperature characteristic and low specific impulse. This polyurethanes binder is obtained from the reaction of rubber binder with isocyanates compound to form urethane linkage and also known as a chain extension reaction. This reaction is important since the network formed exhibit dual functions which are to bind the propellant ingredients together as well as to provide adequate strength related to the propellant mechanical properties.

Amongst rubber binders used in solid propellant application, HTPB is the most widely used from PB family due to their excellent properties compared with other PB binder. The solid rocket propellant is prepared by mixing of HTPB with isophorone diisocyanate (IPDI) for curing process and followed by addition of ammonium perchlorate (AP) and aluminum (Al) powder (Barbieri and Polacco, 2009) according to formulation reported by Aziz (2011). Although the composition of binder used in the production of solid propellant only about ten to fifteen percent (10 – 15%), it does provide significant effect on both chemical and mechanical properties of propellant. Besides that binders also act as a fuel during combustion process since it consists of hydrocarbon chains. A lot of work has been done to improve the properties of HTPB (Toosi *et al.*, 2015, Gupta *et al.*, 2003 and Hocaoglu *et al.*, 2002) and a few studies on finding the new polymer to substitute HTPB (Hagen, 2014, Bluestone *et al.*, 2010, Caro, 2006 and Provatas, 2003).

Recently, extensive research on hydroxyl terminated natural rubber (HTNR) has been done in Propulsion Lab, Universiti Teknologi Malaysia (UTM) in order to find the best formulation to produce HTNR binder with superior properties compared with HTPB (Baharulrazi, 2015, Ab Rasid, 2015, Jaafar, 2014 and Onn, 2014). In their study, deproteinized natural rubber (DPNR) has been used as a raw material to synthesis the HTNR. DPNR is a purified form of NR with lower content of nitrogen and ash. The significance of this purification is to prevent side reaction during degradation process and increases its suitability for specific rubber product purposes (He *et al.*, 2011).

HTNR has been used in many applications especially as an additive in rubber compounding and binder for solid rocket propellant. Similar to HTPB, HTNR contains of hydroxyl end group at both chain ends that useful for chain extension reaction. The reaction of these hydroxyl end groups with isocyanates compound (curing agent) produce urethane network which benefits as a binder for solid rocket propellant application. Moreover, other important characteristics to be considered when dealing with rubber binder is its number average molecular weight ( $M_n$ ). This property has significant effect during mixing process in the preparation of solid

rocket propellant. Therefore, selection of the depolymerization methods and reaction parameter are vital reason in tailoring the  $M_n$  of the rubber binder. Baharulrazi (2015) reported the  $M_n$  of the HTNR produced via oxidative degradation of DPNR using cobalt acetylacetonate (CAA) as an oxidizing agent yielded low molecular weight rubber as HTPB which were 7708 g/mol and 7068 g/mol respectively. Burning rate data shows that HTNR binder has a burning rate of 2.79 mm/s while HTPB binder 2.95 mm/s. Based on the data obtained, the performance of the HTNR seems to be comparable to HTPB binder and suggested as a suitable candidate to substitute HTPB.

Although research on HTNR as a binder for solid rocket propellant is considered as new in UTM, several results have been documented and published by Baharulrazi, (2015), Ab Rasid, (2015), Jaafar, (2014) and Onn, (2014). Toward expending research and development on this field, modified form of NR namely epoxidized natural rubber - 50 (ENR-50) has been chosen to produce hydroxyl terminated epoxidized natural rubber (HTENR) as an alternative rubber binder to replace HTPB binder. ENR-50 is a derivative form of NR that carries the basically almost similar properties with NR. The chemical structure of ENR-50 consists of isoprene and epoxy unit. The presence of epoxy unit makes ENR-50 more resistant towards polar solvent and oil and its compatibility with liquid can be related to the solubility (Gelling, 1991). Due to polarity, ENR-50 is more compatible with tetrahydrofuran (THF) rather than toluene. However, the solubility of ENR in both solvent resulted almost similar percentage of gel content which were 22.9% and 21.3% in toluene and tetrahydrofuran respectively and the addition of small amount of ethanol in toluene did help to decrease the gel content in ENR-50.

Hence, in this work toluene with addition of small amount of ethanol is used as a solvent for synthesis reaction. The selection of ENR-50 as a potential candidate rubber binder for solid rocket propellant is expected to extend the usage of NR with excellent properties likes HTNR based binder and comparable to the commercialize rubber binder which is HTPB.

### 1.3 Problem Statement

Over five decades ago, HTPB has been used as a workhorse in solid rocket propellant application owing to its outstanding mechanical properties (i.e. tensile strength, elongation at break, initial modulus and hardness) and ballistic properties (i.e. burning rate and calorific value). HTPB bearing hydroxyl functional end groups are reacted with curing agent to produce urethane structure that provide structural integrity make it applicable to act as a binder for solid rocket propellant field. HTPB belongs to PB binder family that derived from petrochemicals. Hence, their price is dependent on the oil price and soon their availability may become a major drawback to lengthen its usage. On the other hand, it is difficult to obtain HTPB in a large amount from the manufacturer due to a restriction since this is the important ingredients use in manufacturing a solid rocket propellant. In contrast, NR is renewable natural resources that can be planted regularly and its availability is not a major concern as well as it cultivated continuously. Therefore, it is advantages to utilize NR as an alternative rubber binder to substitute HTPB.

New type of rubber binder from naturally occurred resources has been studied to be used as a binder in composite solid rocket propellant application namely hydroxyl terminated natural rubber (HTNR). Gupta *et al.* (1985) mentioned that HTNR show higher calorific value in contrast to with HTPB thus better ballistic performance. Thomas *et al.* (1992) reported that HTNR had greater advantage over HTPB in terms of the H/C ratio which is 1.6 and 1.5 respectively and had lower initial and peak decomposition temperature which is 250 and 350°C; and 390 and 485°C respectively. However, no extensive research on HTNR as a binder has been reported since their first report. Researcher only focused on the synthesis method to produce telechelic liquid rubber (Ben Saleh *et al.*, 2014, Kwanming *et al.*, 2009 and Dubkov *et al.*, 2006) without concerning the terminal end groups and less was concentrated on the research and development to produce rubber binder for solid rocket propellant.

Owing to that reason, study on the utilization of natural based binder (HTNR) to substitute HTPB seems worthy since Malaysia is amongst the top NR producer, and consumption of natural resources is preferable owing to green technology and low cost of raw materials (Chapman, 2007). HTNR with low molecular weight and viscosity has been used as an additive especially in composite materials and blending system as well as a precursor for the synthesis of new products (Kanestion *et al.*, 2014; Bijarimi *et al.*, 2014; Ben Saleh *et al.*, 2014; Tan *et al.*, 2013; Phetphaisit *et al.*, 2013 and Phinyocheep *et al.*, 2005). Therefore, it seems valuable to expand the general purpose of NR which basically focusing on tire industry (Chapman, 2007) into high impact application such as a binder for rocket propellant application. Meanwhile, by producing our own natural rubber binder it is expected that to be more cost effective than importing it from other countries. In spite of own rubber binder, the consumption of renewable natural resources contributes to give many benefits especially towards reducing the effect of global warming.

Oxidative degradation of deproteinized natural rubber (DPNR) in the presence of ethanol at different reaction time and temperature has been studied to produce HTNR as an alternative rubber binder to substitute HTPB binder in solid rocket propellant application (Baharulrazi, 2015; Ab Rasid, 2015; Jaafar, 2014 and Onn, 2014). Hydroxyl end group is chosen for chain extension reaction to produce rubber binder. The effect of reaction parameter such as reaction temperature, reaction time, type of alcohol used also a very important factor to be evaluated in production of low  $M_n$  liquid rubber. Overall, HTNR is believed as a suitable candidate to substitute HTPB. Towards expanding the research in this area, it was an attempt to synthesis HTENR from ENR-50 rather than DPNR to be used as a rubber binder for solid rocket propellant application. The produced HTENR binder is expected to exhibit almost similar properties as HTNR binder and comparable to HTPB binder.

The selection of ENR is owing to several reasons. Firstly, ENR is derived from the introduction of epoxy group on the NR backbones, thus it contains general characteristic of NR. Its resilience properties are required in binder application especially during transportation and storage of solid rocket propellant. For rubber binder application, suitable resilience value is needed to prevent propellant from damages when its drop from a specific height. Secondly, ENR has similar H/C ratio with NR which is 1.6 that higher than HTPB does with 1.5. Thus the energy store inside the hydrocarbon is high compared with HTPB and it is expected that HTENR binder produced high combustion energy from HTPB binder. Thirdly, the study made by Thitithammawong *et al.* (2011) mentioned that hydroxyl telechelic natural rubber derived from ENR produce higher percent yield (81%) and low molecular weight (850 g/mol) over NR based hydroxyl telechelic natural rubber which are 44% and 4900 g/mol respectively. Based on the aforementioned reason, the chosen of ENR as a starting raw material for binder application is expected to have almost similar properties likes HTPB hence meet the criterion as a rubber binder.

In this study, oxidative degradation using CAA as an oxidizing agent in the presence of ethanol and followed by reduction with sodium borohydride ( $\text{NaBH}_4$ ) was used to produce hydroxyl (OH) terminated end groups. OH end groups were chosen over carbonyl end groups owing to its stability. The produced HTENR bearing OH groups was then used as a binder for the preparation of solid rocket in the making solid rocket propellant. Other ingredients uses for the production of solid rocket propellant were isophorone diisocyanate (IPDI) as a curing agent, ammonium perchlorate (AP) as oxidizer and aluminium powder (Al) as a metal fuel. The performance of HTENR based propellant was studied to compare with the commercial HTPB based propellant in terms of its burning rate and calorific value.

## 1.4 Objectives

The research objectives are as below:

1. To produce HTENR by oxidative degradation of ENR and study the reduction of molecular weight of the degraded ENR by varying the reaction time and the amount of oxidizing agent.
2. To characterize the HTENR obtained and identify the end groups.
3. To perform chain extension reaction of HTENR with IPDI for the formation of polymer network
4. To utilize HTENR in the making of solid rocket propellant and carry out its burning rate and bomb calorimeter test thus compare with HTPB based propellant as a reference.

## 1.5 Scope of Study

The scopes of this research are:

1. Depolymerization of ENR to obtain HTENR with number average molecular weight ( $M_n$ ) below 50,000 g/mol using oxidative degradation method. The effect of reaction parameters on the reduction of molecular weight were study by varied the reaction times from 1, 3, 5 and 20 hours while the amounts of oxidizing agent were varied from 1% w/w, 2% w/w, 3% w/w, 4% w/w and to 5% w/w.

2. The characterizations of HTENR were done using GPC, FTIR and NMR. HTENR with lowest molecular weight was chosen as rubber binder for solid rocket application. GPC was used to determine the molecular weight of respected HTENR. Meanwhile, FTIR and NMR were used for structure and end group determination.
3. The ability of HTENR to perform chain extension reaction was evaluated by reaction of HTENR with IPDI as a curing agent.
4. HTENR based propellant was prepared by mixed with curing agent, oxidizer and fuel and the ability of HTENR as a binder for solid rocket propellant was monitored by burning rate test and bomb calorimeter test.



## 5.2 Recommendation for Future Work

Oxidative degradation of ENR using 3% w/w of CAA as an oxidizing agent at 60°C for five hours reaction and followed by the treatment with sodium borohydride yielded HTENR with  $M_n$  and  $M_w$  of 37000 g/mol and 102000 g/mol respectively. Although HTENR was successfully produced to be functioned as a binder for composite solid rocket propellant, further work need to be carried out to fully explore its potential characteristics. For future work, it is recommended to carry out the degradation of ENR at various reaction temperatures to evaluate its degradation rate. This is because the reaction temperature contributes a significant effect on the degradation rate to minimize the recombination rate. Increase in the degradation rate whilst decrease in recombination rate can lead to the production of low molecular weight HTENR which is the main intention for a rocket binder.

In order to improve the performance of HTENR propellant, it is suggested that other types of diisocyanates is used as a curing agent to further study their suitability as well as varying the NCO/OH ratio to find the best ratio for propellant mixtures. The addition of chain extender is suggested for future work to improve the miscibility between binder, curing agent, oxidizer and metal fuel. Moreover, AP is a major ingredient in propellant thus their size may have a huge effect on burning rate and mechanical strength. Therefore, the size of AP should be varied to identify the effect on HTENR based propellant. The curing time is another important parameter to be studied on since the uncured and over cured propellant sample may have affect on its performance.

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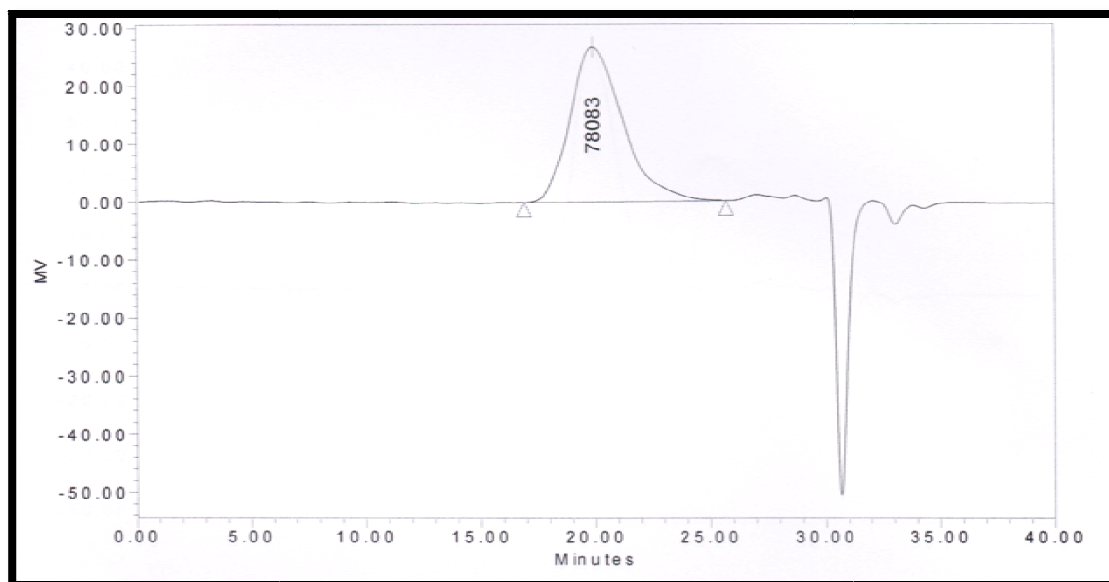
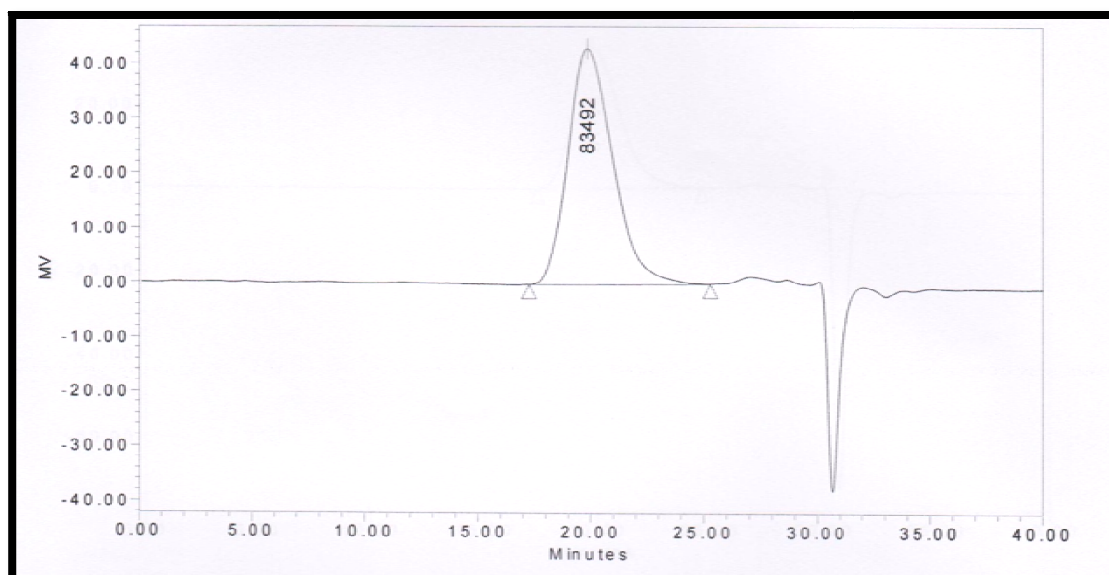


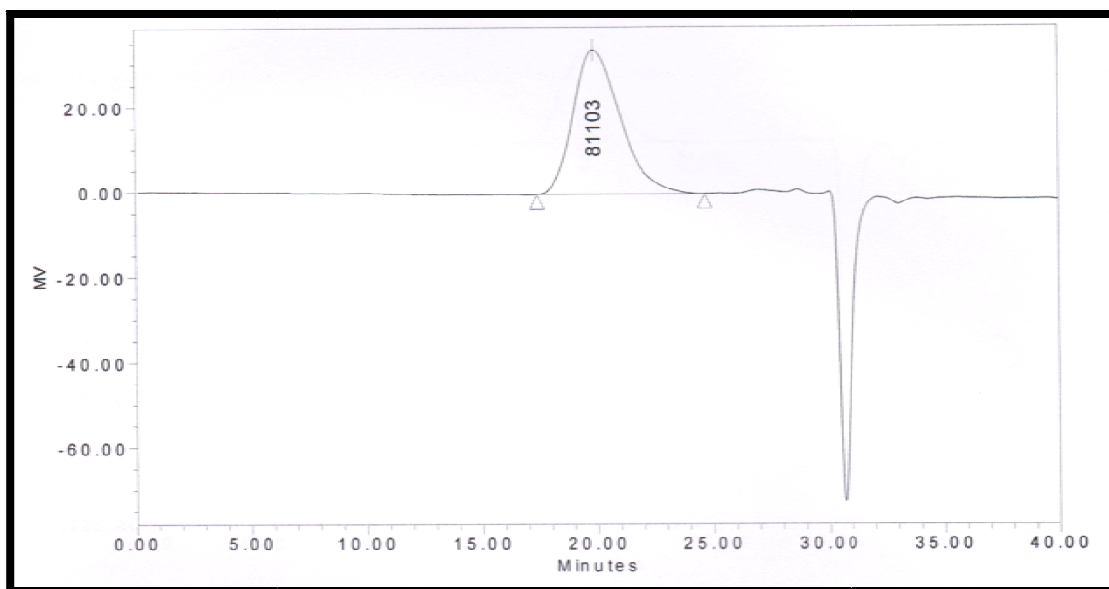
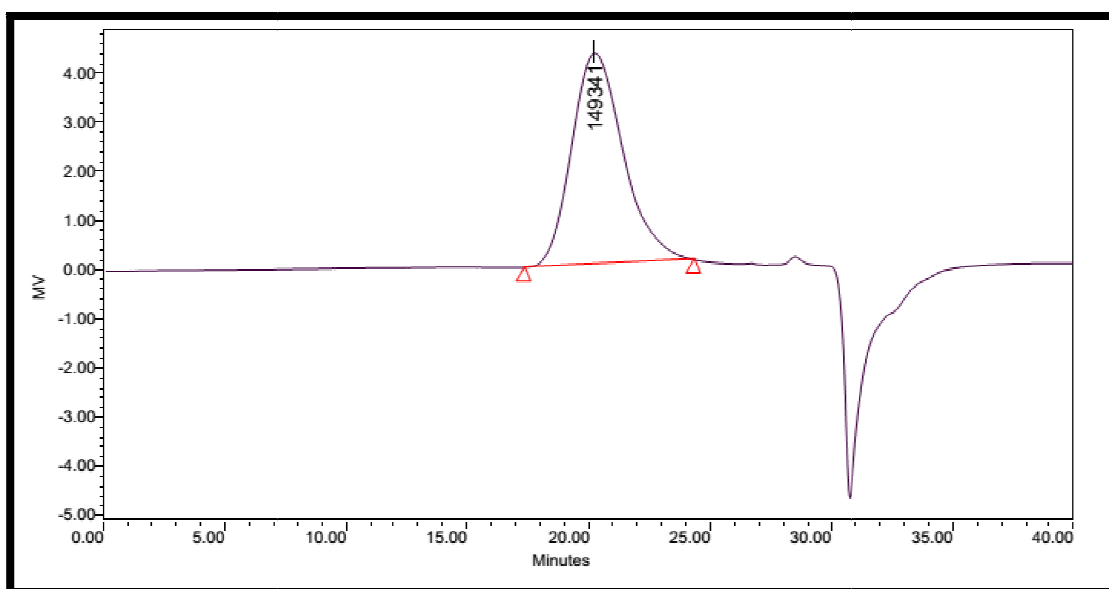
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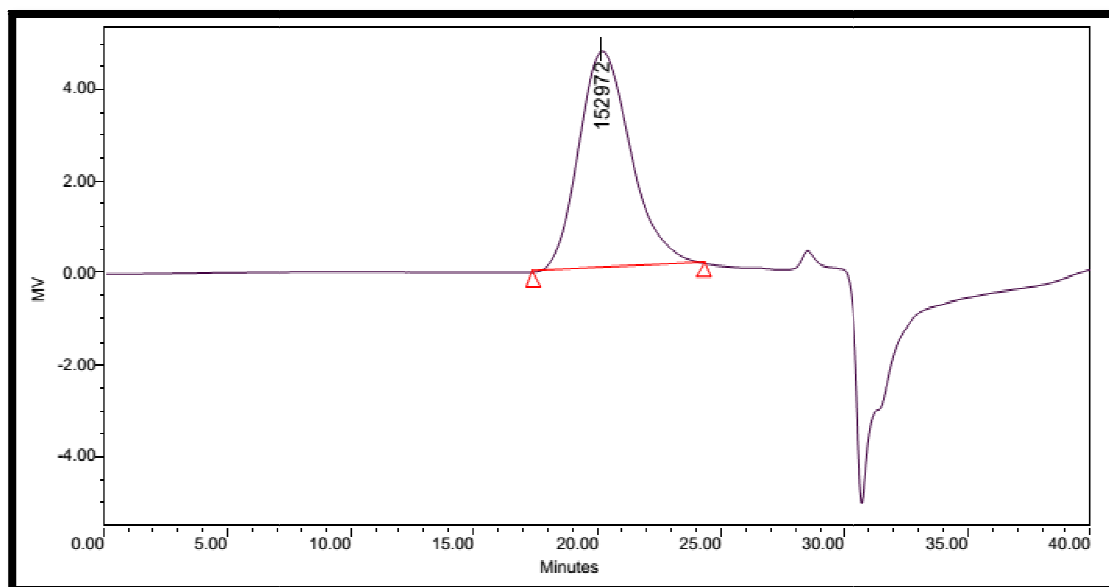
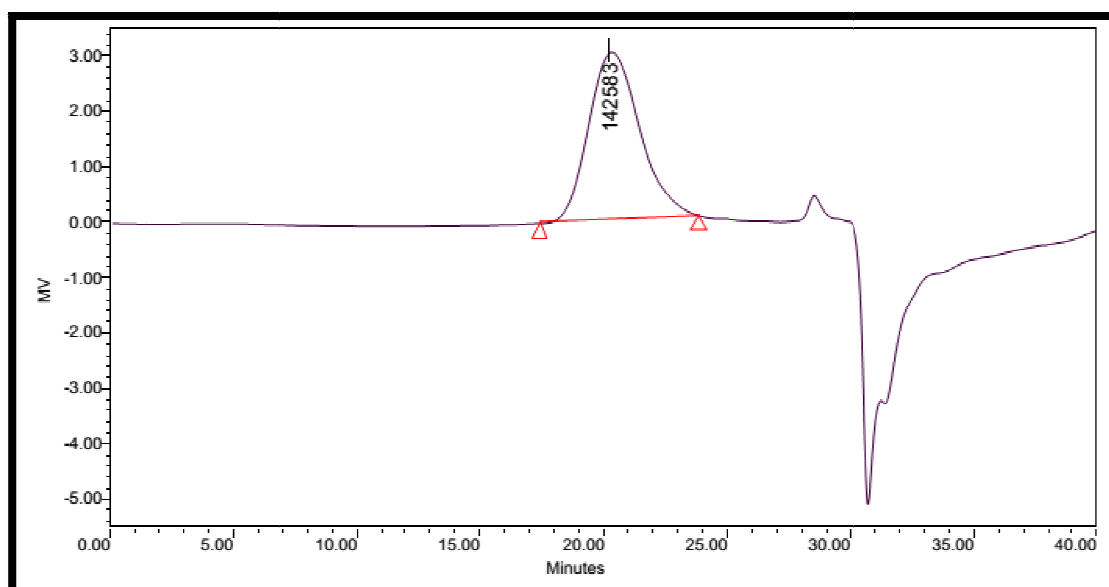
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**Chromatogram of HTENR 3CE5** $M_n$  37000 g/mol ;  $M_w$  102000 g/mol**Chromatogram of HTENR 4CE5** $M_n$  48000 g/mol ;  $M_w$  101000 g/mol

**Chromatogram of HTENR 5CE5** $M_n$  45000 g/mol ;  $M_w$  95000 g/mol**Chromatogram of HTENR 6CE5** $M_n$  70000 g/mol ;  $M_w$  137000 g/mol

**Chromatogram of HTENR 8CE5** $M_n$  73000 g/mol ;  $M_w$  140000 g/mol**Chromatogram of HTENR 10CE5** $M_n$  75000 g/mol ;  $M_w$  133000 g/mol

## APPENDIX E

### Calculation of the ratio epoxy over double bond

Ratio of integral area from  $^1\text{H}$  NMR spectrum of ENR (before oxidative degradation);

$$\left[ \frac{I_{2.7}}{I_{5.1}} \right] = \frac{1.143}{1}$$

$$= \underline{1.143}$$

Ratio of integral area from  $^1\text{H}$  NMR spectrum HTENR (after oxidative degradation);

$$\left[ \frac{I_{2.7}}{I_{5.1}} \right] = \frac{2.253}{1}$$

$$= \underline{2.253}$$

$$\therefore \frac{2.253}{1} = \frac{1.143}{x}$$

$$x = \frac{1.143 \times 1}{2.253}$$

$$x = \underline{0.507}$$



## APPENDIX F

## Burning Rate Test Data

Sample	No	Time(s)	Burning rate (mm/s)	Average (mm/s)	Calorific Value
HTPB	1	15.91	3.14	2.95	15143
	2	16.28	3.07		
	3	17.45	2.87		
	4	18.33	2.73		
HTENR-1	1	25.00	2.00	2.14	12691
	2	22.00	2.27		
	3	25.00	2.00		
	4	22.00	2.27		
HTENR-3	1	23.00	2.17	2.06	14765
	2	29.00	1.72		
	3	27.00	1.85		
	4	20.00	2.5		
HTENR-5	1	20.00	2.5	2.26	13545
	2	23.00	2.17		
	3	24.00	2.08		
	4	22.00	2.27		